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(54) **Method for the mechanical working of cast iron and an aqueous concentrate to be used in the method.**

(57) Mechanical working of cast iron performed in the presence of an aqueous metal working composition containing a copper complex and corrosion inhibitor. An aqueous concentrate, which after dilution with water is suitable for application in mechanical working of cast iron, is also described.

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METHOD FOR THE MECHANICAL WORKING OF CAST IRON AND AN AQUEOUS CONCENTRATE TO BE USED IN THE METHOD.

The present invention relates to a method for the mechanical working of cast iron, especially of so called nodular or spheroidized iron. The working is performed in the presence of an aqueous metalworking composition containing a copper complex and a corrosion inhibitor. The invention further comprises an aqueous concentrate, which after dilution with water could be used in a method for mechanical working of cast iron.

Metalworking fluid compositions are well known in the art. From e.g. the US Patent 4 129 509 it is known to use a mineral oil and water containing fluid emulsion. In order to stabilize the oil and water emulsion against attacks from bacteria and against degradation due to the metalworking conditions the patent suggests the addition of an emulsifying agent and a metal complex of a heavy metal ion and a polyfunctional organic ligand. However, mineral oil containing cutting fluids causes problems when used for machining of metals due to the formation of undesirable non-settling and highly viscose sludge in storage tanks, pumps and tubing. The presence of emulsifying agents aggravates this problem further. Thus, it is well known from prior art that mineral oil-containing cutting fluids for this reason are particularly unsuitable for use in the machining of cast iron, which produces large amounts of particulate contaminations.

Mechanical working of cast iron, especially of the quality usually called nodular or spheroidized graphite iron, is often performed in the presence of aqueous oilfree metalworking compositions such as the ones disclosed in the US Patent 3 265 620. In connection herewith a poisonous gas is generated, i.e. phosphine. The generation of gas depends on the fact that cast iron contains carbon (graphite) with inclusions of phosphorous material. When machining cast iron

in the presence of water, this phosphorous material reacts under the formation of phosphine.

To reduce the generation of phosphine it has therefore been suggested for e.g. cutting operations to use metalworking compositions containing potassium permanganate which is a strong oxidizing agent. Even if this method has proved to reduce the generation of phosphine, the consequences, however, are severe corrosion attacks on machinery, tools, and machined iron. Furthermore, the compositions containing potassium permanganate are not stable, resulting in precipitations, primarily in the form of manganese ore.

For the mechanical working of cast iron it has now according to the present invention proved possible to use aqueous, stable compositions which prevent the formation of phosphine and which at the same time have good corrosion inhibiting and cooling properties. This is achieved by machining cast iron in the presence of an alkaline aqueous composition containing Cu^{2+} bound as a complex. Suitable pH-range is 8-10. More specifically, the aqueous composition according to the invention contains

a) an organic copper(II)complex, the content of copper complex being 0.05-2, preferably 0.1-1 % of the weight of the composition

b) a conventional corrosion inhibitor in the amount of 0.1-5, preferably 0.2-3 % of the weight of the composition. Normally and preferably the composition in accordance with the invention has the form of a clear solution.

It is very surprising that a composition according to the present invention very effectively prevents the formation of phosphine, since the content of free Cu^{2+} in such a system will be extremely low. The use of a complexing agent prevents

precipitation of copper, and Cu^{2+} will be available as oxidizing agent. It is very important that the bivalent copper ions in a metalworking composition are available in the form of an organic chelate with sufficient complex stability in order to prevent the bonding of copper to other components in the composition, such as corrosion inhibitors and lubricants. It has namely been found that the corrosion protection is reduced if the corrosion inhibitor forms a complex with the copper ions. Furthermore, in case that Cu^{2+} is precipitated e.g. depending on precipitations with corrosion inhibitors, lubricants, or other components present, a metalworking composition with low phosphine inhibiting ability is obtained. The complexing agent must therefore have an ability to form complex with Cu^{2+} which is at least equivalent with the ability of other components introduced in the metal working composition, such as corrosion inhibitors and lubricants.

Complexing agents according to the present invention are polyvalent carboxylic acids, like oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid and fumaric acid; hydroxycarboxylic acids, like citric acid and tartaric acid; aminocarboxylic acids, like nitrilotriacetic acid (NTA), propylenediaminetetraacetic acid (PDTA) and ethylenediaminetetraacetic acid (EDTA); and alkanolamines, e.g. triethanolamine and diethanolamine. Especially suitable are complexing agents having a stability constant for the 1:1-complex with Cu^{2+} within the range of 10^3–10^{17}, and preferably within the range of $5 \cdot 10^3$–10^{15}. Examples of such preferred complexing agents are citric acid, nitrilotriacetic acid and triethanolamine.

The corrosion inhibitors suitable for use according to the invention are components normally used for corrosion inhibition of iron within the metalworking area and containing at least one hydrophilic group. Suitable inhibitors are organic amines, e.g. alkanolamines, alkylamines, cyclic amines and

polyamines; phosphate esters; carboxylic acids and other components having good corrosion inhibiting properties on iron. Some of the corrosion inhibitors, like triethanolamine, has also the ability to form a complex with copper. These special compounds can thus be applied in the function of corrosion inhibitors as well as of complexing agents, but they must be added in such amounts that they can accomplish both their functions. A suitable amount of complexing agents is 0.04-3 % by weight of the composition. Especially preferred corrosion inhibitors according to the present invention is alkylarylsulfonamidocarboxylic acids, morpholine, triethanolamine or phosphate esters, like those with the general formula

$$RO(AO)_n - \underset{\underset{O}{\|}}{\overset{OR_1}{\overset{|}{P}}} - OM$$

where R is a hydrocarbon group with 12-24 carbon atoms, AO is an alkyleneoxy with 2-3 carbon atoms, n is 0-10, preferably 1-6, M is hydrogen or a monovalent cation, and R_1 has the meaning of M or R.

A composition with excellent properties is obtained, if triethanolamine, nitrilotriacetic acid or citric acid is chosen as complexing agent and used together with a conventional iron corrosion inhibitor like alkylarylsulfonamidocarboxylic acids, morpholine and/or phosphate esters in combination with triethanolamine as corrosion inhibitors.

If desired, the aqueous composition according to the instant invention may also contain a lubricant provided that the lubricant does not, in any considerable amount, form precipitations with Cu^{2+}. Preferably the composition is essentially free from hydrocarbon components. Examples of suitable lubricants are conventional lubricants of the type monocarboxylic acid, alkyl- or alkylarylsulphonates or -sulphates, alkylphosphates, alkylphosphonates, alkyl-

(polyoxyalkylene)phosphates or polyalkylene glycols. Many of these lubricants have also an excellent corrosion inhibiting capacity. The amount of lubricant may suitably be in the range of 0.03-3 % by weight of the aqueous composition.

Besides complexing agents, corrosion inhibitors and lubricants, the aqueous metalworking composition may also contain pH-regulating agents, bactericides, perfumes, viscosity modifying agents and solubilizing agents well known per se. The solubilizing agents are normally low-molecular hydroxylic compounds, like monoethylethyleneglycol, propyleneglycol, butyldiethyleneglycol and ethyleneglycol.

When preparing a metalworking composition according to the invention it is advisable first to prepare a concentrate, the preparation of which may be made by adding, to a suitable amount of water, a water-soluble salt, like copper(II)acetate, complexing agents and corrosion inhibitors. After this the other components are added under slight stirring. The amount of water in relation to other components is chosen in such a way that a water content of about 10-70 % by weight of the concentrate is obtained. Typical formulations of the concentrate according to the invention are as follows:

Cu^{2+}-complex	1-50, preferably 2-30 % by weight
with a Cu^{2}-content of	0.5-20, preferably 1-10 % by weight
Corrosion inhibitor	1-50, preferably 2-30 % by weight
Lubricant	0.50, preferably 1-30 % by weight

pH-regulators, bactericides, solubilizing agents, etc	0-20, preferably 0-10 % by weight
Water	10-70, preferably 20-50 % by weight

Before application the concentrate is diluted with water in order to obtain a working solution with a water content of 99.5-85 % by weight.

The invention is illustrated by the following examples:

Example

A number of concentrates were prepared by adding copper(II)-acetate to water and thereafter corrosion inhibitors and lubricants according to the table below. The concentrates were then diluted with water to obtain an amount corresponding to ten times their own weight. Compositions A and B are comparison compositions. The composition B has a formulation in accordance with the US Patent 4 129 509.

Composition	Components	Content, weight %
1	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	4.0
2	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	0.8
	Alkylphenylsulfonamido-carboxylic acid	0.45
	Water	Rest
3	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	0.8
	Alkylphenylsulfonamido-carboxylic acid	0.45
	Morpholine	1.8
	Water	Rest

4	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	0.8
	C_{18}-alkyldi(propylene-oxy)phosphate	2.2
	Water	Rest
5	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	2.6
	Pelargonic acid	0.5
	Water	Rest
6	Cu^{2+}-acetate · H_2O	0.1
	NTA	0.1
	C_{18}-alkyldi(oxypropylene) phosphate	0.75
	Triethanolamine	0.25
	Water	Rest
7	Cu^{2+}-acetate · H_2O	0.25
	NTA	0.25
	C_{18}-alkyldi(oxypropylene)-phosphate	0.75
	Triethanolamine	0.25
	Water	Rest
8	Cu^{2+}-acetate · H_2O	0.5
	NTA	0.5
	C_{18}-alkyldi(oxypropylene)-phosphate	0.75
	Triethanolamine	0.25
	Water	Rest
9	Cu^{2+}-acetate · H_2O	1.0
	NTA	1.0
	C_{18}-alkyldi(oxypropylene) phosphate	1.5
	Triethanolamine	0.5
	Water	Rest

10	Cu^{2+}-acetate · H_2O	0.5
	Triethanolamine	0.8
	Citric acid (monohydrate)	0.6
	C_{18}-alkyldi(oxypropylene) phosphate	1.6
	Water	Rest
A	Potassium permanganate	1.0
	Triethanolamine	0.5
	C_{18}-alkyldi(oxypropylene) phosphate	1.2
	Water	Rest
B	Organomet (Cu^{2+}-acetate) from Coolant Control Inc.	0.1
	Mineral Oil	5.0
	Water	Rest

5 g of nodular iron chips produced by dry turning were placed in a test glass having a piece of cotton on bottom. 3 ml of one of the fluid compositions above was poured over the chips and the test glass was placed into a water bath at 80°C. After a reaction time of 5 minutes 1 liter air was pumped through the test glass and the amount of phosphine in the air was measured by passing the air through an analysis tube containing a reagent being coloured by phosphine (Dräger phosphine 0.1/a). The tube was graded from 0 to 4 ppm for an air amount of 1 liter.

The same type of iron chips were also used for a corrosion test. This was carried out by placing 30 g chips on a filter paper in a Petri-dish containing 1.25 ml of the fluid. After 24 hours the corrosion was determined by placing a transparent film with a grid over the filter paper and the occurence of corrosion was determined for every point of intersection on the grid. The corrosion was determined as the ratio between the points of intersection with corrosion and the whole number

of points of intersection. The following results were obtained.

Test	ppm phosphine	% corrosion
1	0.1	8
2	less than 0.1	6
3	0.1	4
4	0.1	0
5	0.1	5
6	0.6	0
7	0.4	0
8	0.1	0
9	0.1	2
10	0	0
A	0.5	more than 20
B	3.0	not measured

From the results it is evident that the released amount of phosphine by applying the method according to the invention is very low. If the working had been performed without the presence of a phosphine reducing component, the amount of phosphine would have been about 3 ppm. The corrosion test shows that the compositions 1-10 also cause a remarkably low corrosion.

CLAIMS

1. Method for the mechanical working of cast iron, the mechanical working being performed in the presence of an alkaline aqueous composition containing an iron corrosion inhibitor and, if so desired, a lubricant, characterized in that the aqueous composition contains

a) an organic copper(II)complex, the amount of copper complex being 0.05-2 percent by weight of the weight of composition and

b) the iron corrosion inhibitor in a content of 0.1-5 percent by weight.

2. Method according to claim 1, characterized in that the complexing agent included in the copper(II)complex has a stability constant for the 1:1-complex with Cu^{2+} of 10^3-10^{17}, preferably $5 \cdot 10^3$-10^{15}.

3. Method according to claim 1 or 2, characterized in that the complexing agent is citric acid, nitrilotriacetic acid, triethanolamine or mixtures thereof.

4. Method according to claim 1-3, characterized in that the iron corrosion inhibitor is an alkylarylsulfonamido-carboxylic acid, morpholine, triethanolamine, a phosphate ester or a mixture thereof.

5. Method according to claim 3, characterized in that the corrosion inhibitor at least partly consists of a combination of triethanolamine and one or more corrosion inhibitors from the group consisting of alkylarylsulfonamido-carboxylic acid, morpholine and phosphate ester.

6. Concentrate, which after dilution with water, is suitable to be used in mechanical working of cast iron

according to claim 1-5, characterized in that it contains the following components.

Cu^{2+}-complex	1-50, preferably 2-30 % by weight
with a Cu^{2}-content of	0.5-20, preferably 1-10 % by weight
Corrosion inhibitor	1-50, preferably 2-30 % by weight
Lubricant	0.50, preferably 1-30 % by weight
pH-regulators, bactericides, and solubilizing agents	0-20, preferably 0-10 % by weight
Water	10-70, preferably 20-50 % by weight

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EUROPEAN SEARCH REPORT

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Application number

EP 84850008.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Y	EP-A-0 025 236 (METALLGESELLSCHAFT AG) & US-A-4 289 547 * Claims 1, 8, 9; page 7, lines 7-29 *	1-6	C 10 M 3/00
Y,D	US-A-3 265 620 (D. HEIMAN) * Claims 1, 7; column 1, lines 40-54; column 2, lines 30-42 *	1-6	
Y,D	US-A-4 129 509 (NATIONAL RESEARCH LABORATORIES) & SE-A-7709144-5 DE-A-2 738 040 * Claims 1, 3, 8, 10; column 7, lines 57-62 *	1-6	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 10 M
Y	US-A-4 199 381 (METALLGESELLSCHAFT AG) & SE-A-7808658-4 DE-A-2 736 874 * Claim 1 *	3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
STOCKHOLM	10-05-84	HEDLUND, J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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